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Synthesis of three-dimensional ordered mesoporous MnO₂ and its catalytic performance in formaldehyde oxidation

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ABSTRACT

Three-dimensional (3D) ordered mesoporous MnO₂ was prepared using KIT-6 mesoporous molecular sieves as a hard template. The material was used for catalytic oxidation of HCHO. The material has high surface areas and the mesoporous characteristics of the template, with cubic symmetry (ia3d). It consists of a β -MnO₂ crystalline phase corresponding to pyrolusite, with a rutile structure. Transmission electron microscopy and X-ray photoelectron spectroscopy showed that the 3D-MnO₂ catalyst has a large number of exposed Mn⁴⁺ ions on the (110) crystal plane surfaces, with a lattice spacing of 0.311 nm; this enhances oxidation of HCHO. Complete conversion of HCHO to CO₂ and H₂O was achieved at 130 °C on 3D-MnO₂; the same conversions on α -MnO₂ and β -MnO₂ nanorods were obtained at 140 and 180 °C, respectively, under the same conditions. The specific mesoporous structure, high specific surface area, and large number of surface Mn⁴⁺ ions are responsible for the catalytic activity of 3D-MnO₂ in HCHO oxidation.

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Manganese oxides, including MnO, MnO₂, Mn₂O₃, and Mn₃O₄, are important in a range of applications such as ion exchange, molecular adsorption, catalysis, electrochemical reactions, batteries, and magnetic processes, because of their structural flexibility and novel chemical and physical properties [1–5]. Three-dimensional (3D) ordered mesoporous MnO₂ has disordered polycrystalline walls and a unit cell parameter of 20.85 nm; it has a large number of exposed (110) crystal planes, with a lattice spacing of 0.311 nm, and more Mn⁴⁺ ions are present on these than on other planes [6]. 3D-MnO₂ has been used as an effective environmentally friendly material for ethanol, carbon monoxide, benzene, and toluene oxidation, and in electronic components [6–9]. The catalytic oxidation of volatile organic

compounds (VOCs) over 3D-MnO₂ shows the potential usefulness of this novel material. It has excellent hydrophobicity and a strong affinity toward VOCs, and can selectively adsorb VOC molecules and oxidize VOCs to CO₂ and H₂O even in the presence of water vapor [10,11].

The development of effective catalysts for complete oxidation of low concentrations of HCHO at low temperatures is still a challenge. In this study, an ordered mesoporous 3D-MnO₂ material was synthesized using a nanocasting method, and its catalytic performance in HCHO oxidation was evaluated. This work was motivated by the fact that HCHO is becoming a major indoor pollutant. It is emitted from widely used construction and decorating materials, and long-term exposure to indoor air

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containing even a very low concentration of HCHO is potentially harmful to human health [12,13].

The 3D-MnO₂ was prepared using KIT-6 mesoporous silica as a hard template [11,13]. After KIT-6 sample was synthesized, KIT-6 molecular sieves (4.0 g) were added to a solution of Mn(NO₃)₂·4H₂O in ethanol (0.91 mol/L, 40 mL). The sample was evaporated to dryness at 80 °C and calcined at 200 °C for 6 h. These casting and evaporating steps were repeated. Finally, the material was calcined at 400 °C for 6 h. The KIT-6 hard template was removed using a NaOH solution (2 mol/L). Centrifugal separation was used to remove sodium silicate, and the samples were dried at 100 °C and calcined at 400 °C to yield 3D-MnO₂. 3D-MnO₂ grain growth is related to the initial crystallite size of the KIT-6 template and calcination temperature [2]; for example, 3D-Mn₂O₃ can be obtained by increasing the calcination temperature.

α-MnO₂ and β-MnO₂ nanorods were prepared using the method reported in the literature [14]. MnSO₄·H₂O (0.008 mol) and an equal amount of (NH₄)₂S₂O₈ were added to distilled water at room temperature to form a homogeneous solution. The solution was transferred to a 40-mL Teflon-lined stainless-steel autoclave, and the autoclave was sealed and maintained at 140 °C for 12 h. After the reaction was complete, the solid product was filtered, washed with distilled water to remove any ions in the final product, and dried at 120 °C to yield β-MnO₂. α-MnO₂ was prepared by adding analytical grade (NH₄)₂SO₄ (0.015 mol) to the reaction system.

Powder X-ray diffraction (XRD) was performed using a TTR3 X-ray diffractometer with a Cu K_α radiation source, at a scanning speed of 0.05°/min, 40-kV tube voltage, and 40-mA tube current. The pore size distribution and N₂ adsorption-desorption isotherms of the sample were investigated using an Autosorb-1MP instrument. Transmission electron microscopy (TEM) was performed using a JEM-2011 instrument at a voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-5300 instrument at 300 W, with Mg K_α X-rays as the excitation source. HCHO oxidation tests were performed in a fixed-bed quartz-tube reactor (φ10 mm) using 0.2 g of catalyst (40–60 mesh). HCHO gas was generated and injected using a N₂ bubbler in a low-temperature thermostatic bath at 0 °C; the N₂ was passed through a container filled with formalin (a HCHO aqueous solution (37%)). The total gas flow rate through the reactor was kept at 100 mL/min using

mass-flow meters; the gas consisted of 400 ppm HCHO, 20% of O₂, and balance N₂. The space velocity was 30000 mL g⁻¹ h⁻¹. The reaction products were detected online using an Agilent 7890A gas chromatograph, with a thermal conductivity and mass-selective detector connected to Porapak-Q and HP-INNOWAX columns, respectively. No carbon products other than CO₂ were detected.

Fig. 1(a) shows the N₂ adsorption-desorption isotherms. The isotherm has a hysteresis ring and is a type IV adsorption isotherm; this indicates the presence of mesopores [9,13]. Fig. 1(b) shows the Barrett-Joyner-Halenda pore size distribution of 3D-MnO₂ calculated from the desorption isotherm. The 3D-MnO₂ pore size distribution is 3.7–11.4 nm, therefore the material has a mesoporous structure. 3D-MnO₂ has a high specific surface area (87 m²/g), which is consistent with previous literature reports [6].

Fig. 2 shows the XRD patterns of 3D-MnO₂. The low-angle diffraction peaks at 2θ = 1.00° and 1.04° correspond to the (211) and (332) planes (Fig. 2(a)), indicating that 3D-MnO₂ has the 3D ordered mesoporous structure with cubic symmetry (ja3d) of its template. The wide-angle diffraction peaks at 2θ = 28.7°, 37.3°, 42.8°, 56.7°, 59.4°, 64.8°, and 72.3°, corresponding to the (110), (101), (111), (211), (220), (002), and (301) planes, respectively, are attributed to the crystalline phase of β-MnO₂ pyrolusite [8,9]. This indicates that the 3D-MnO₂ has a rutile structure.

Fig. 3 shows TEM images of 3D-MnO₂, and α-MnO₂ and β-MnO₂ nanorods. The α-MnO₂ (Fig. 3(c)) and β-MnO₂ (Fig. 3(d)) nanorods are both nonporous materials, and have one-dimensional single-crystal nanostructures of diameters about 10 and 100 nm, respectively. The α-MnO₂ nanorod diameter is much smaller than that of the β-MnO₂ nanorods. Ordered mesoporous structures can be clearly observed in Fig. 3(a) and (b). The 3D-MnO₂ has exposed (110) crystal planes with a lattice spacing of 0.311 nm. In the β-MnO₂ unit cell, more Mn⁴⁺ ions are exposed on the (110) crystal planes than on the other planes [15,16]. The different structures of the samples may result from the different amounts of Mn⁴⁺ exposed on the (110) crystal facets.

Fig. 4 shows that the Mn 2p_{2/3} XPS profiles have two components, at binding energy of 641.6 and 642.9 eV, corresponding to surface Mn³⁺ and Mn⁴⁺ ions, respectively. The peak areas indicate that the surface Mn⁴⁺/Mn³⁺ molar ratios for 3D-MnO₂,

Fig. 1. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of 3D-MnO₂.

Fig. 2. Low-angle (a) and wide-angle (b) XRD patterns of 3D-MnO₂.

and α -MnO₂ and β -MnO₂ nanorods are 3.9, 3.1, and 1.6, respectively. These results show that larger numbers of Mn⁴⁺ species are exposed on the 3D-MnO₂ surface. This large number of Mn⁴⁺ ions provides sufficient active sites for HCHO oxidation, as previously reported [6].

Fig. 5 shows the HCHO conversions over 3D-MnO₂, and α -MnO₂ and β -MnO₂ nanorods. 3D-MnO₂ is a promising catalyst and has the best oxidation activity, entirely converting HCHO to CO₂ and H₂O at 130 °C. Complete conversions of HCHO over α -MnO₂ and β -MnO₂ nanorods were achieved at 140 and 180 °C, respectively. The catalytic activity of 3D-MnO₂ is therefore better than that of α -MnO₂ and β -MnO₂ nanorods, indicating that the catalyst morphology has a significant effect on the catalytic activity. The specific mesoporous structure, higher specific surface area, and larger number of surface Mn⁴⁺ ions of 3D-MnO₂ are responsible for its good catalytic activity in HCHO oxidation. 3D-MnO₂ has a special pore channel structure and high surface area, which are beneficial to the adsorption and diffusion of reactants and products, and the large number of

Mn⁴⁺ ions exposed on the (110) facets provide sufficient active sites for HCHO oxidation. In addition, the oxidation performance over 3D-MnO₂ is similar to that previously reported for a 3D-Co₃O₄ catalyst [13], and is better than that of CeO₂ nanospheres and Ag-supported CeO₂ bulk particles [17]. These results indicate that 3D-MnO₂ has good potential as an efficient catalyst for HCHO removal. Further investigations on the optimum preparation and possible metal-doping of 3D-MnO₂ are in progress.

Fig. 4. Mn 2p_{3/2} XPS profiles of 3D-MnO₂, and α -MnO₂ and β -MnO₂ nanorods.

Fig. 3. TEM images of (a, b) 3D-MnO₂, and (c) α -MnO₂ and (d) β -MnO₂ nanorods.

Fig. 5. Catalytic activities in HCHO oxidation over (1) 3D-MnO₂, and (2) α -MnO₂ and (3) β -MnO₂ catalysts.

Graphical Abstract

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Three-dimensional ordered mesoporous MnO₂ was synthesized using KIT-6 molecule sieves as a hard template. The material showed high catalytic activity in formaldehyde oxidation and has good development potential.

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三维有序介孔二氧化锰制备及其甲醛催化氧化性能

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摘要: 空气中的甲醛主要来源于化工、建材、涂料、装潢材料以及机动车尾气。甲醛具有光化学活性, 对人体具有致癌致畸作用。高浓度甲醛对人体健康和空气环境危害极大, 室内低浓度甲醛对人体也有很大伤害。因此, 消除室内、机动车尾气以及工业生产过程中的甲醛非常必要。目前, 去除甲醛的方法主要有吸附法、光催化法和催化燃烧法。其中, 催化燃烧法具有去除效率高、起燃温度低、适用范围广、设备操作简单以及无二次污染等优点, 因而非常适用于去除高浓度和低浓度甲醛。该方法的核心是催化剂的制备和筛选。近年来, 用于甲醛催化燃烧的催化剂主要是负载型贵金属和金属氧化物。由于贵金属催化剂成本较高, 所以金属氧化物催化剂备受关注。MnO₂种类繁多, 既包括人工合成的棒状、线状、管状、球状和孔状等形貌, 还包括自然界存在的α、β、γ和δ等类型。其中, 介孔MnO₂因具有较大的比表面积和特殊的孔道而应用于乙醇、甲苯、苯等挥发性有机物的催化氧化反应。目前, 尚未见三维(3D)有序介孔MnO₂催化氧化甲醛的报道。

本文以合成的3D有序介孔KIT-6分子筛为硬模板剂, 采用纳米浇筑法制备出3D有序介孔MnO₂材料。为了比较, 采用水热法合成了α-MnO₂和β-MnO₂纳米棒。采用X射线粉末衍射、N₂吸附-脱附、透射电子显微镜和X射线能谱(XPS)等方法对催化剂进行了表征。在微型固定床石英管反应器上评价了催化剂催化甲醛氧化活性, 采用气相色谱(GC)联接热导检测器

(TCD)和质谱检测器(MSD)检测产物和反应物的含量.

表征结果表明,3D-MnO₂复制了KIT-6硬模板的三维有序立方对称介孔结构(ia3d),且具有金红石型 β -MnO₂晶相,属软锰矿,具有较大的比表面积和双孔分布介孔结构,最大孔径分别位于3.7和11.4 nm处. 3D-MnO₂样品具有清晰的孔道结构,而 α -MnO₂和 β -MnO₂纳米棒为无孔的一维纳米单晶材料. 另外,3D-MnO₂表面暴露了较多的(110)晶面,有利于增加表面Mn⁴⁺离子. XPS结果证实3D-MnO₂表面存在较多的Mn⁴⁺离子,这些Mn⁴⁺离子为甲醛催化反应提供了丰富的活性位,有利于提高甲醛氧化活性. 评价结果表明,3D-MnO₂具有良好的低温催化性能,于130 °C即可将甲醛完全转化成CO₂和H₂O;而在同样条件下, α -MnO₂纳米棒和 β -MnO₂纳米棒分别在140和180 °C才能完全转化甲醛. 3D-MnO₂具有良好的甲醛催化性能主要归因于特殊的介孔结构、较大的比表面积和较多的表面Mn⁴⁺离子.

关键词: 三维有序材料; 介孔结构; 二氧化锰; 甲醛; 催化氧化

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